



RESEARCH ARTICLE

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Optimization of lead adsorption of mordenite by response surface methodology: characterization and modification

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Abstract

Background: In order to remove heavy metals, water treatment by adsorption of zeolite is gaining momentum due to low cost and good performance. In this research, the natural mordenite was used as an adsorbent to remove lead ions in an aqueous solution.

Methods: The effects of adsorption temperature, time and initial concentration of lead on the adsorption yield were investigated. Response surface methodology based on Box-Behnken design was applied for optimization. Adsorption data were analyzed by isotherm models. The process was investigated by batch experiments; kinetic and thermodynamic studies were carried out. Adsorption yields of natural and hexadecyltrimethylammonium-bromide-modified mordenite were compared.

Results: The optimum conditions of maximum adsorption (nearly 84 percent) were found as follows: adsorption time of 85-90 min, adsorption temperature of 50°C, and initial lead concentration of 10 mg/L. At the same optimum conditions, modification of mordenite produced 97 percent adsorption yield. The most appropriate isotherm for the process was the Freundlich. Adsorption rate was found as 4.4. Thermodynamic calculations showed that the adsorption was a spontaneous and an exothermic process.

Conclusions: Quadratic model and reduced cubic model were developed to correlate the variables with the adsorption yield of mordenite. From the analysis of variance, the most influential factor was identified as initial lead concentration. At the optimum conditions modification increased the adsorption yield up to nearly 100 percent. Mordenite was found an applicable adsorbent for lead ions especially in dilute solutions and may also be applicable in more concentrated ones with lower yields.

Keywords: Risk, Environment, Hazard, Lead, Adsorption

Background

Heavy metals are defined as those having higher density than 5000 g/L [1]. When their concentrations reach a certain level, they cause serious damage to the environment, animals and public health. Lead is one such extremely toxic element even at low concentrations that can damage to the nervous system, gastrointestinal tract, reproductive system, liver and brain [2,3]. Major industries of lead pollution are mining, paint, chemical, textile etc. [4]. Lead discharge from them to the atmosphere is

approximately 2000 kilotons/year; thus lead pollution is serious environmental problems of worldwide. There are conventional methods for removing lead from aqueous solution such as reverse osmosis, ion exchange, electrochemical treatment, solvent extraction, chemical precipitation, adsorption and biosorption [5,6]. Among those, adsorption is a simple process with low cost and good performance [7]. High exchange capacity, high specific surface area and low cost make natural zeolites good adsorbents [8,9]. Their adsorption capacity can also be further increased by modification with various agents, such as CTAB (cetyltrimethylammoniumbromide) and HDTMA (hexadecyltrimethylammonium-bromide) [9]. A special type of zeolite, mordenite is abundant in nature. Comparing

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to other zeolites, it has rather low Si/Al ratio (5:1) which may render the adsorption of lead [10]. Removal of heavy metal ions by using mordenite is very rare [11-14]. None of the studies investigated the effect of modification of mordenite on adsorption yield. Above studies have shown that lead removal by mordenite is strongly dependent upon the initial concentration of lead and adsorption conditions. In assessing the effect (single effect and interactive effects) of variables on quality attributes an adequate experimental design is required. Response Surface Methodology (RSM) has an important application for analyzing effects of several independent variables and also interactive effects among the variables on the response. Nevertheless, no study has been found in the literature for optimization of adsorption of lead ions by mordenite, neither modified nor unmodified. The objective of the present research was to optimize the adsorption conditions of lead ions by mordenite. It was thought that the level of adsorption may be further increased by modification of mordenite with HDTMA. The effects of variables including initial lead concentration, adsorption time and temperature on adsorption yield were investigated by three-variable-three-level Box-Behnken Design (BBD). Empirical model correlating response to the three variables was then developed. Langmuir and Freundlich isotherm models were investigated in terms of their appropriateness and fractional-life method was used to determine kinetic parameters. The thermodynamic parameters of the process were also calculated.

Methods

Chemicals and reagents

Mordenite, a type of zeolite, was selected for having high ion-exchange capacity, high surface area and low Si/Al ratio. Mordenite, analytical grades of lead nitrate ($\text{Pb}(\text{NO}_3)_2$) and HDTMA were purchased from Sigma and used without further purification. Three stock lead nitrate solutions (10 mg/L, 1005 mg/L, and 2000 mg/L) were prepared and used in adsorption studies as working solutions.

Analysis and measurements

Elemental analysis of natural mordenite was determined by Perkin-Elmer (2400 series) Elemental Analyzer. The surface area of mordenite was determined by BET analysis of Micromeritics (Gemini 2360). The concentrations of residual lead(II) ions in the supernatant solutions were determined using ICP-OES (Perkin-Elmer Optima 5300 DV) measurements.

Design of experiments, model fitting and statistical analysis

The optimum condition for the adsorption of lead by mordenite was determined by means of BBD and RSM. RSM is a collection of statistical and mathematical

techniques useful for evaluation of relationship existing between a number of controlled experimental factors and measured responses according to one or more selected criteria [15,16]. Optimization studies were carried out by studying the effect of three variables including initial lead ion concentration, adsorption temperature and time. The chosen independent variables in this study were coded according to Eq. (1):

$$X_i = \frac{X_i - X_0}{\Delta X} \quad (1)$$

where x_i is the dimensionless coded value of the i th independent variable, x_0 is the value of x_i at the center point and Δx is the step change value. The behavior of the system is explained by the following empirical second-order polynomial model (Eq. 2):

$$Y = \beta_0 + \sum_{i=1}^k \beta_i x_i + \sum_{i=1}^k \beta_{ii} x_i^2 + \sum_{i=1}^{k-1} \sum_{j=2}^k \beta_{ij} x_i x_j + \varepsilon \quad (2)$$

where Y is the predicted response, x_1, x_2, \dots, x_k are the input variables, which affect the response Y , $x_i^2, x_j^2, \dots, x_k^2$ are the square effects, β_0 is the intercept term, $x_i x_j, x_j x_k$ and $x_i x_k$ are the interaction effects, β_i ($i = 1, 2, \dots, k$) is the linear effect, β_{ii} ($i = 1, 2, \dots, k$) is the squared effect, β_{ij} ($j = 1, 2, \dots, k$) is the interaction effect and ε is a random error [17-19].

The Design-Expert 8.0 (Stat-Ease Inc., Minneapolis MN, USA) software was used for regression and graphical analysis of the experimental data to fit the equations developed and for evaluation of their statistical significance. BBD is frequently used under RSM design. The study carried out involved the employment of BBD to optimize the adsorption process due to its suitability to fit quadratic surface that usually works well for process optimization. Design of 15 experiments consisting of three replicates at the central points was employed to the second-order polynomial model. The optimum values of the selected variables were obtained by solving the regression equation at desired values of the process responses as the optimization criteria. Each of the parameters was coded at three levels: -1, 0, and +1. The range of variables was decided on the basis of pre-experimental values. The range and level of the variable in coded units for RSM studies were given in Table 1.

Each experiment was repeated three times (average values were used in optimization) and the experimental sequence was randomized in order to minimize the effects of the uncontrolled factors.

Lead adsorption studies

Fifteen batch adsorption experiments designed by RSM were conducted with 0.50 g of mordenite (dried in an oven at 60°C for 24 h) at agitation speed of 200 rpm and

Table 1 Experimental ranges and levels of the independent variables

Independent variables	Range and level		
	-1	0	+1
Adsorption time, min (X_1)	30	75	120
Adsorption temperature, °C (X_2)	20	35	50
Initial lead ion concentration, mg/L (X_3)	10	1005	2000

the initial pH of working solution. Each experiment was carried out in Erlenmeyer flasks containing 100 ml lead (II) solution at determined temperature in an isothermal shaker. Samples were withdrawn at the end of the determined contact time and filtered through 0.25 μ m filters. Filtered samples were analyzed for residual lead ion concentration. Natural mordenite particles were modified according to the reaction with 100 ml of HDTMA solution (0.05 M) at 30°C in a reactor containing 5 g mordenite particles and magnetically stirred for 3 h. At the end of the reaction, zeolite particles were separated by filtration, washed several times with distilled water and dried in an oven at 60°C for 24 h. Same adsorption procedure was applied to HDTMA-mordenite except that the conditions chosen as the optimum of unmodified one. Metal removal by mordenite was determined according to Eq. (3):

$$R = \frac{P_0 - P_e}{P_0} \times 100 \quad (3)$$

where R is the percentage of lead adsorbed by adsorbent, P_0 is the initial concentration of metal ion in mg/L and P_e is the final concentration of metal ion in mg/L.

Adsorption isotherms

In order to diagnose the nature of adsorption (homogeneous or heterogeneous) onto the mordenite the equilibrium adsorption isotherms are required. Two theoretical isotherm models, namely Langmuir (applicable to homogeneous adsorption) and Freundlich (applicable to heterogeneous adsorption) isotherms, were used to fit the adsorption data obtained at 35°C. For Langmuir isotherm [20]:

$$\frac{C_e}{Q} = \frac{1}{Q_0 b} + \frac{C_e}{Q_0} \quad (4)$$

where C_e is the equilibrium concentration (mg/L), Q is the amount of metal adsorbed (mg/g), b is sorption constant (L/mg) (at 35°C) related to the energy of sorption, and Q_0 is the maximum sorption capacity (mg/g). For Freundlich isotherm [20]:

$$Q_e = K_F C_e^{1/n} \quad (5)$$

where Q_e is the amount of metal adsorbed at the equilibrium (mg/g), K_F ((mg/g)(L/mg)^{1/n}) and n (dimensionless)

are Freundlich constants related to the adsorption capacity and adsorption intensity, respectively. The regression analysis and calculation of constants of Eq. (4) and (5) were achieved by using the solver add-in function of MS Excel.

Adsorption kinetics

The adsorption data obtained with 1005 mg/L initial lead ion concentration were then fitted to the fractional-life method [21]:

$$t_F = \frac{F^{1-n} - 1}{k(n-1)} C_{A0}^{1-n} \quad (6)$$

where F is the fractional value (C_A/C_{A0}) in time t_F ; n the reaction order; k reaction rate constant; and C_A the concentration of reactant A (mg/L) at time t (min). Kinetic parameters of adsorption were determined by plotting $\log t_F$ versus $\log C_{A0}$ and using MS Excel.

Adsorption thermodynamics

Since temperature is an important parameter effecting both adsorption capacity of mordenite and transport/kinetic process of lead adsorption, the thermodynamic parameters of the process such as enthalpy (ΔH°), entropy (ΔS°), and free energy (ΔG°) of lead adsorption on mordenite were calculated by using following thermodynamic relations [19,22]:

$$\Delta G^\circ = -RT \ln K_c^0 \quad (7)$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (8)$$

Combining these to relations:

$$\ln K_c^0 = \frac{\Delta S^\circ - \Delta H^\circ}{R} * \frac{1}{T} \quad (9)$$

where R is universal gas constant (8.314 Jmol⁻¹ K⁻¹), T is the temperature (K) and K_c is the equilibrium constant at that temperature calculated by the equation:

$$K_c = \frac{C_a}{C_e} \quad (10)$$

where C_a is the concentration of the adsorbed material (mg/L), and C_e is the concentration of remaining material in solution (mg/L).

Results

Properties of natural and modified mordenite

Natural mordenite has a purity of 99.8 percent with impurity of magnesium. According to the chemical composition of the zeolite, the chemical formula was determined as $K_{2.87}Ca_{1.43}Na_{1.27}Al_{7.98}Si_{40}O_{88} \cdot 25H_2O$. This result showed that the major components of mordenite were silica and alumina and the ratio of Si/Al was 5.215. The surface area of the mordenite was determined as 53 m²/g with BET

analysis. HDTMA-modification was corrected with the elemental analysis [23]. The ratio of C/N for HDTMA-mordenite showed that 4.15 percent of modifying agent was transferred onto the surface of the zeolite.

Regression model and optimization

The coded and actual values of the test variables and lead removal percentage were summarized in Table 2. Predicted values for yield by using quadratic model and reduced cubic model were summarized in Tables 3 and 4, respectively. The statistical significance of the quadratic and reduced cubic models was evaluated by analysis of variance (ANOVA) as presented in Table 5 and 6, respectively.

According to the statistical analysis, the empirical relationship in coded units obtained by RSM was as follows:

$$Y = 48.42 + 4.20x_1 + 10.71x_2 - 8.64x_3 + 0.28x_1x_2 - 3.60x_1x_3 - 8.44x_2x_3 - 1.02x_1^2 - 1.26x_2^2 + 8.55x_3^2 - 8.29x_1^2x_2 + 0.99x_1^2x_3 - 3.11x_1x_2^2 \quad (11)$$

where Y is lead ion removal (response) in percentage, x_1 , x_2 and x_3 are the coded values of variables; adsorption time in min (x_1), adsorption temperature in °C (x_2), and initial lead ion concentration in mg/L (x_3).

The results of regression analysis on reduced cubic model are given in Table 7. The significant of each coefficient was determined by F-values and p-values (Table 7). The larger the magnitude of the F-values and the smaller p-values, the more significant is the corresponding coefficients. Values of

Table 3 Observed and predicted values for the quadratic model

Run no	Observed values	Predicted value	Residual
1	55.800	57.850	-2.05
2	83.500	78.860	4.64
3	71.400	70.340	1.06
4	49.350	45.700	3.65
5	48.498	48.420	0.079
6	47.190	49.780	-2.59
7	48.373	48.420	-0.046
8	48.900	46.850	2.05
9	44.530	41.940	2.59
10	48.385	48.420	-0.034
11	45.200	48.850	-3.65
12	49.930	55.630	-5.70
13	42.915	37.210	5.70
14	47.700	48.760	-1.06
15	44.800	49.440	-4.64

“prob > F” less than 0.0500 also indicated high significant regression at 95 percent confidence level. According to the F- and p-values, adsorption temperature and initial ion concentration were found more effective on the adsorption process. Figure 1 shows the simultaneous effects of adsorption temperature (a) and initial lead ion concentration (b) on lead removal efficiency.

In the numerical optimization desirability function was used. In order to determine the usability of mordenite in low and high concentrated lead solutions, time and

Table 2 Experimental design matrix based on Box-Behnken and results

Run no	Independent variables						Observed values
	Coded values			Real values			
1	-1	0030	-1	30	35	10	55.800
2	0	+1	-1	75	50	10	83.500
3	+1	0	-1	120	35	10	71.400
4	0	+1	+1	75	50	2000	49.350
5	0	0	0	75	35	1005	48.498
6	-1	+1	0	30	50	1005	47.190
7	0	0	0	75	35	1005	48.373
8	+1	0	+1	120	35	2000	48.900
9	+1	-1	0	120	20	1005	44.530
10	0	0	0	75	35	1005	48.385
11	0	-1	-1	75	20	10	45.200
12	+1	+1	0	120	50	1005	49.930
13	-1	-1	0	30	20	1005	42.915
14	-1	0	+1	30	35	2000	47.700
15	0	-1	+1	75	20	2000	44.800

Table 4 Observed and predicted values for the reduced cubic model

Run no	Observed values	Predicted value	Residual
1	55.800	55.800	0.000
2	83.500	83.500	0.000
3	71.400	71.400	0.000
4	49.350	49.350	0.000
5	48.498	48.420	0.078
6	47.190	47.190	0.000
7	48.373	48.420	-0.047
8	48.900	48.900	0.000
9	44.530	44.530	0.000
10	48.385	48.420	-0.035
11	45.200	45.200	0.000
12	49.930	49.930	0.000
13	42.915	42.920	0.005
14	47.700	47.700	0.000
15	44.800	44.800	0.000

Table 5 Analysis of variance (ANOVA) for the quadratic model

Source of variations	Degrees of freedom	Sum of squares	Mean square	F-value	Probability (p)
Regression	9	1560.78	173.42	5.46	0.0381
Main effects	3	931.37	931.37	29.31	0.2419
Square effects	3	279.68	279.68	8.80	0.7422
Interaction effects	3	336.93	336.93	10.60	0.9244
Residual	5	158.89	31.78		
Total	14	1719.67			

R^2 : 0.9076, adjusted R^2 : 0.7413, predicted R^2 : -0.4783, lack of fit: 11134.81, CV: 10.89.

temperature were set within range, and level of lead removal was set at maximum in each criteria (Table 8). Initial lead ion concentration was set as different targets for maximum desirability. By seeking from several starting points for each criteria, the best local maximums for each were obtained and summarized in Table 8.

Characterization of adsorption

In the present study, Langmuir and Freundlich isotherm models [20] were applied to the experimental data to determine the type of adsorption (homogeneous, heterogeneous). The adsorption constants of each isotherm were summarized in Table 9. According to those, the value of R^2 so lower than 1, demonstrating that Langmuir isotherm is not applicable for describing the adsorption. The experimental data fitted well to Freundlich Model ($R^2 = 0.993$) which shows that mordenite has a form of surface heterogeneity [20].

The adsorption kinetics was determined by fractional-life method choosing the fractional value of 0.8 [21]. The reaction rate was 4.39 at 0°C for 1005 mg/L of initial

Table 6 Analysis of variance (ANOVA) for the reduced cubic model

Source of variations	Degrees of freedom	Sum of squares	Mean square	F-value	Probability (p)
Regression	12	1719.66	143.30	30129.29	<0.0001
Main effects	3	828.02	828.02	174087.1	<0.0001
Square effects	3	279.68	279.68	58801.17	0.0012
Interaction effects	3	336.93	336.93	70836.5	0.0147
Added terms	3	158.88	158.88	33404.44	0.0024
Total	14	1719.67			

R^2 : 1.000, adjusted R^2 : 1.000, CV: 0.13.

Table 7 Regression analysis for the reduced cubic model

Model term	Coefficient estimate	Standart error	F-Value	p-Value
Intercept	+48.42	0.04	30129.29	<0.0001
x_1	+4.20	0.034	14834.96	<0.0001
x_2	+10.71	0.034	96509.35	<0.0001
x_3	-8.64	0.034	62742.79	<0.0001
x_1x_2	+0.28	0.034	66.52	0.0147
x_1x_3	-3.60	0.034	10899.15	<0.0001
x_2x_3	-8.44	0.034	59870.83	<0.0001
x_1^2	-1.02	0.036	807.59	0.0012
x_2^2	-1.26	0.036	1227.48	0.0008
x_3^2	+8.55	0.036	56766.10	<0.0001
$x_1^2x_2$	-8.29	0.049	28924.08	<0.0001
$x_1^2x_3$	+0.99	0.049	410.05	0.0024
$x_1x_2^2$	-3.11	0.049	4070.31	0.0002

lead concentration (Figure 2) and the rate constant was calculated as $3.75 \cdot 10^{-14} \text{ min}^{-1}(\text{mg/L})^{-3.39}$.

The thermodynamics of adsorption of lead on mordenite was studied at temperatures of 20, 35, and 50°C. The change in Gibbs free energy (ΔG°), enthalpy (ΔH°), and entropy (ΔS°) values were obtained by using Eq. (9) and the results were summarized in Table 10.

Discussion

In order to develop an equation describing the relation between the adsorption yield and three adsorption variables shown in Table 2, a BBD was conducted. Quadratic model and reduced cubic model were developed to correlate the variables to the response. Predicted values for yield by using reduced cubic model (Table 4) were closer to observed values than those by using quadratic model (Table 3). In quadratic model (Table 5), F-value of the model 5.46 implied that the model was statistically significant. There was only a 3.81 percent chance that a model F-value this large could occur due to noise. The fit of the model was checked by the determination coefficient (R^2). In this case, the value of the determination coefficient ($R^2 = 0.9076$) indicated that 9.24 percent of the total variable was not explained by the model. The value of adjusted determination coefficient (adjusted $R^2 = 0.7413$) was low and it was not in reasonable agreement with the adjusted R^2 . Negative predicted R^2 implied that the overall mean was a better predictor of the response than the current model. Significant lacks of fit and high value of the coefficient of variation were found. Probability values (greater than 0.1000) indicated that some of the model terms are not significant. But, reduced cubic model (Table 6) produced the closest predicted values, predicted R^2 and adjusted R^2 equal to 1,

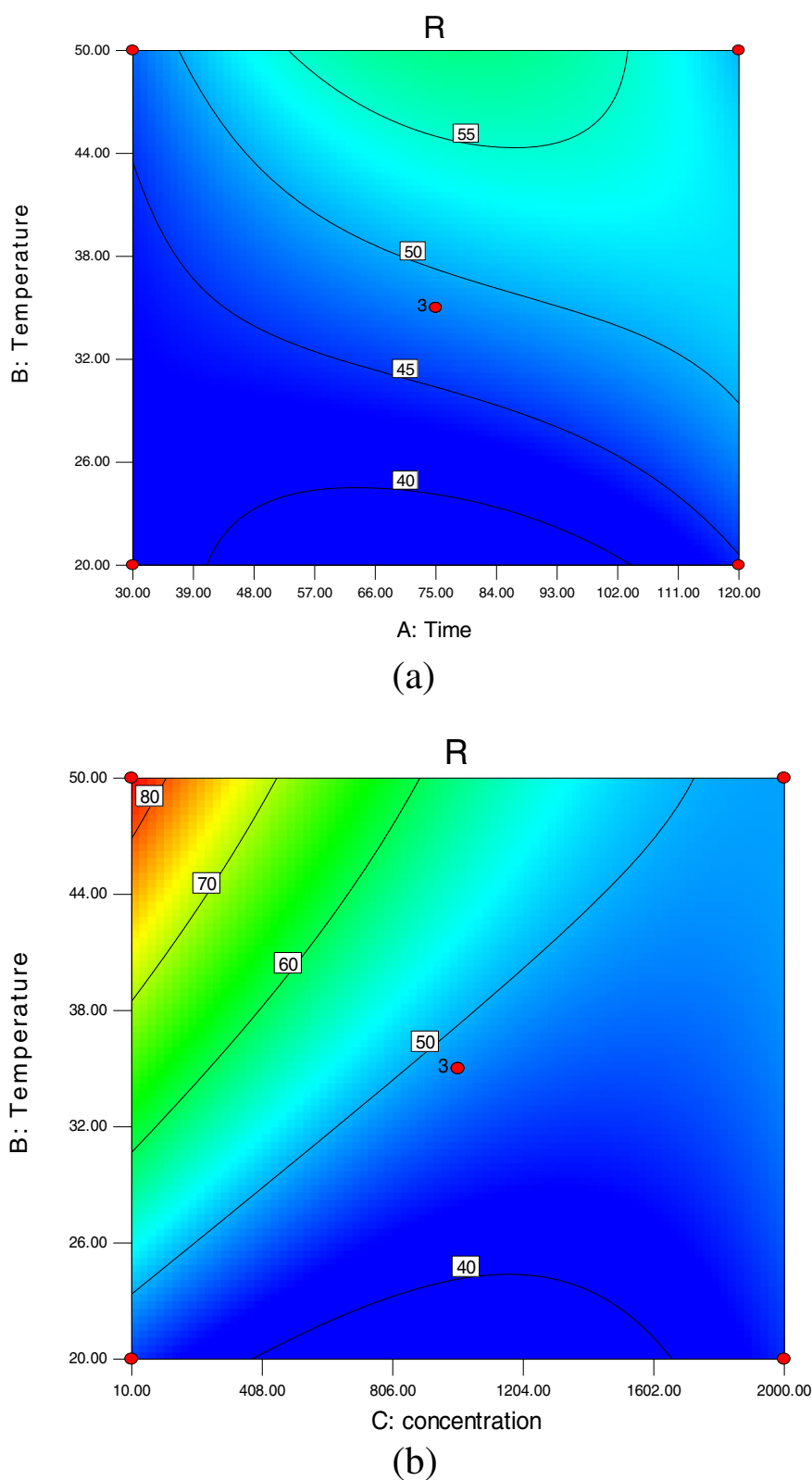


Figure 1 Contour plots for the effect of (a) adsorption temperature (°C) and adsorption time (min); (b) adsorption temperature (°C) and initial lead ion concentration (mg/L) on the lead removal (black-and-white form).

Table 8 Numerical optimization of the model obtained by desirability function

Criteria	Solution	Desirability
1 Adsorption time: in range	89.47	1.000
Adsorption temperature: in range	49.68	
Initial lead concentration: target = 10	10.00	
Lead removal: maximize	83.7369	
2 Adsorption time: in range	85.29	0.968
Adsorption temperature: in range	50.00	
Initial lead concentration: target = 100	100.00	
Lead removal: maximize	81.0066	
3 Adsorption time: in range	81.83	0.602
Adsorption temperature: in range	50.00	
Initial lead concentration: target = 1000	799.10	
Lead removal: maximize	61.8751	
4 Adsorption time: in range	82.66	0.425
Adsorption temperature: in range	50.00	
Initial lead concentration: target = 2000	828.11	
Lead removal: maximize	61.2467	

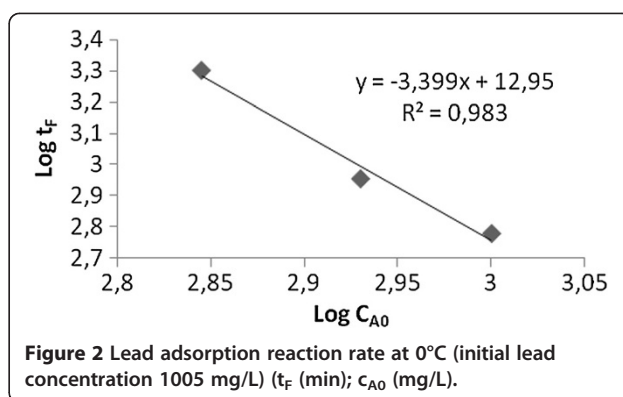
no lack of fit and low coefficient of variance. The model F-value implied that the model was significant, and there was only a 0.01 percent chance occurs due to noise. Thus, as a result of the statistical analysis, reduced cubic model was found satisfactory for describing the process and useful for developing empirical relation.

Lead removal showed to be very sensitive to changes in the temperature both in dilute and in concentrated solutions. The removal capacity of mordenite was sharply increased when the adsorption temperature increased from 20 to 50°C in dilute solutions; as it was also reported by Wang [14] (from 20 to 40°C; in a solution of 40 mg lead/L). No comparison can be made with the research by Dai *et al.* [13] since the temperature set constant at 25°C. For moderately concentrated solutions (1005 mg/L) this increase in yield was only 5 percent. The increase in yield due to increase in adsorption temperature in diluted solutions was more dominated than one in concentrated solutions.

Initial lead ion concentration was another parameter that has high effect on the response. As can be seen on Figure 1, the concentration of the aqueous solution increases the removal of lead decreases. About 84 percent

Table 9 Isotherm model constants for the adsorption of lead on mordenite (T: 35°C, sorbent dosage: 0.5 g, initial lead concentration: 10–2000 mg/L)

Langmuir model			Freundlich model		
Q_0 (mg/g)	b (L/mg)	R^2	$1/n$	K_F	R^2
4.387	0.0006	0.571	0.876	0.0041	0.993



yield was obtained in diluted solutions (10 mg/L). When the initial lead concentration increased to 100 mg/L, the yield decreased to 81 percent. Dai *et al.* [13] also observed that increase in initial lead concentration from 3 to 200 mg/L decreased the lead removal down to 70 percent. Also (Figure 1), the results of the study showed that this yield could also be achieved up to 500 mg/L of initial lead concentrations.

Adsorption time has little effect on lead removal. It was found that nearly 80–90 minute was enough to obtain highest yield in both dilute and concentrated solutions. The results obtained were in agreement with the work done by Dai [13] which reported that optimum time required to reach the equilibrium was 100 min. Also Wang [14] reported that adsorption time has little effect on yield and that the adsorption required 90 min.

Optimum conditions for the adsorption process were searched by numerical optimization section of the software by choosing different targets for initial lead ion concentration. As shown in Table 8, for dilute solutions (initial lead ion concentration up to 10 mg/L), the best local maximum was found to be at adsorption time of 85–90 min, adsorption temperature of 50°C, lead removal of nearly 84 percent, and desirability of 1.000. High desirability shows that the estimated function may represent the experimental model and desired conditions. As the concentration increases, desirability and lead removal percentage were found to be decreasing (Table 8). Finally, 97 percent lead adsorption was achieved by using HDTMA-mordenite at the same optimum conditions of unmodified-mordenite; i.e. initial lead ion concentrations: 10–100 mg/L. It can be concluded that,

Table 10 Thermodynamical constants of lead adsorption at different temperatures

T (°C)	K_c^0	ΔG^0 (kJ/mol)	ΔS^0	ΔH^0
20	0.791	571.44		
35	1.683	−1333.70	15.91	−4737
50	3.55	−3403.87		

modification of mordenite or adjustment of adsorption medium (lowering up to pH 3) [13] produce nearly the same adsorption yield. But lowering the pH of the medium was useful for solutions containing 3 mg lead /L [13], whereas modification of mordenite was applicable up to 100 mg/L of lead solutions.

Fitting of adsorption data showed that (Table 9), Langmuir isotherm, thus monolayer adsorption, solely, was not suitable for the process. Equilibrium adsorption data were best represented by the Freundlich isotherm. Heterogeneous adsorption of lead on mordenite was also stated in the literature before [14]. The obtained value of $(1/n)$ ($0.1 < 1/n < 1$) demonstrated that favourable nature of both lead and the heterogeneity of the mordenite sites. The $1/n$ value of the present study was higher than those obtained (0.537 at 30°C; 0.555 at 40°C) [14] showing that higher adsorption intensity of the mordenite used. Negative Gibbs free energy (Table 10) indicated the spontaneous nature of adsorption at those temperatures. These results were well-matched with literature [14]. Also, negative ΔH° values showed the adsorption of lead ions was an exothermic process. A negative enthalpy values were also reported for the adsorption of lead ions onto wollastonite, bentonite and mordenite [14]. A positive ΔS° value corresponded to an increase in both the randomness at the solid-solution interface and the degree of freedom of the adsorbed species. Adsorption reaction rate was found 4.4 at 0°C (Figure 2). In a different study, lead adsorption data (at 20–40°C) onto a local mordenite were fitted well to several equations; pseudo-second order, parabolic diffusion and Elovich equations [14]. It seemed that the steps of adsorbate transport from the solution to the surface of mordenite; such as film diffusion, pore diffusion, surface diffusion and adsorption are strongly affected on temperature.

Conclusions

A Box-Behnken Design was conducted to study the effects of three adsorption variables, namely adsorption time, temperature and initial lead ion concentration on the adsorption yield of lead. Quadratic model and reduced cubic model were developed to correlate the variables to the response. Through the analysis of response surfaces, adsorption temperature and initial lead ion concentration were found to have significant effects on adsorption yield, whereas initial ion concentration showed that most significant. Process optimization was carried out and the experimental values were found to agree satisfactorily with the predicted values. Mordenite was shown to be a promising adsorbent for removal of lead from aqueous solutions. Further increase in the adsorption yield obtained at the optimum conditions was achieved with HDTMA-modification. Adsorption isotherm, adsorption kinetic and adsorption thermodynamics

were studied. Equilibrium adsorption data were best represented by the Freundlich isotherm model. Thermodynamic calculations indicated that the adsorption was exothermic and spontaneous process.

Competing interests

The authors declared that they have no competing interests.

Authors' contributions

HT carried out part of the experimental studies. TK carried out part of the experiments and participated in the design of the study. SYY performed the statistical analysis, conceived of the study, and participated in its design and coordination and helped to prepare the manuscript. All authors read and approved the final manuscript.

Acknowledgements

The present research was funded under the code of 2635-YL-11 by Scientific Research Project Coordination Unit of Suleyman Demirel University (Turkey).

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Received: 28 August 2012 Accepted: 6 October 2013

Published: 6 January 2014

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doi:10.1186/2052-336X-12-5

Cite this article as: Turkeyilmaz et al.: Optimization of lead adsorption of mordenite by response surface methodology: characterization and modification. *Journal of Environmental Health Science & Engineering* 2014 **12**:5.

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